3,5-二硝基水杨酸和菲咯啉构筑的两个镧配合物的合成、晶体结构及荧光性质

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摘要:以 3,5-二硝基水杨酸(H_2dns)和菲咯啉(phen)为配体合成了 2 个新的镧配合物[$La_2(dns)_2(Hdns)_2(phen)_4$] (**1**)和[$La_4(dns)_6(phen)_6$] (**2**),并对它们进行了红外分析、元素分析、热重分析和单晶结构分析。单晶衍射结果表明,配合物 **1** 和 **2** 均为三斜晶系,$P\bar{1}$ 空间群。配合物 **1** 和 **2** 中 La(Ⅲ)通过配体 H_2dns 桥联分别形成双核结构和四核结构。热重和荧光分析表明:**2** 热稳定性高于 **1**,**1** 和 **2** 均在 467 nm 处有最强荧光发射强度。

关键词:La(Ⅲ)配合物;3,5-二硝基水杨酸;晶体结构;荧光性质
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Syntheses, Crystal Structures and Luminescence Properties of Two La(Ⅲ) Complexes Assembled by 3,5-Dinitrosalicylic Acid and 1,10-Phenanthroline

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Abstract: Two new complexes based on 3,5-dinitrosalicylic acid (H_2dns) and 1,10-phenanthroline (phen), namely [$La_2(dns)_2(Hdns)_2(phen)_4$] (**1**) and [$La_4(dns)_6(phen)_6$] (**2**) have been synthesized and characterized by IR, elemental analyses, thermogravimetric analyses and X-ray diffraction technique. Single-crystal X-ray diffraction analyses revealed that two complexes all crystallize in the triclinic system and space group $P\bar{1}$. For complexes **1**, H_2dns ligands adopt tridentate and didentate coordination modes to link La(Ⅲ) ions into dinuclear structure. However H_2dns ligands adopt tridentate coordination mode to link La(Ⅲ) ions into tetranuclear structure. TG and fluorescence analysis show the thermal stability of **2** is higher than that of **1**, and **1** and **2** have same maximum emission band of the fluorescence at 467 nm. CCDC: 1856530, **1**; 1856531, **2**.

Keywords: La(Ⅲ) complexes; 3,5-dinitrosalicylic acid; crystal structures; luminescent properties

Recently, a large number of lanthanide compounds with different organic ligands have been documented due to their abundant properties like fluorescence and magnetism[1-5]. As well as we know, the judicious selection of the organic ligands plays very important role in the structural and functional information of

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such target complex materials[6-8]. To be sure, ligands containing oxygen or oxygen and nitrogen atoms, especially multi-carboxylate or multi-hydroxyl ligands are usually used in the architectures of supramolecular compounds. In this aspect, 3,5-dinitrosalicylic acid (H_2dns) was usefully selected to construct molecular polymers or clusters because of its intrinsic nature, such as having more coordination sites, good rigidity and suitable acidity[9-12]. However, there are very few examples of rare earth compounds involving H_2dns[13]. Taking account of the above, we selected La_2O_3 to react with H_2dns, and 1,10-phenanthroline (phen) was introduced as auxiliary ligand to the La_2O_3/H_2dns systems. We obtained two new La(Ⅲ) complexes. In addition, thermal stabilities and the luminescent properties of the complexes have also been investigated.

1 Experimental

1.1 Materials and methods

All starting reagents were of AR grade and used as purchased without further purification. Analyses of C, H and N were determined on a Perkin-Elmer 240 Elemental analyzer. IR spectrum was recorded as KBr discs on a Shimadzu IR-408 infrared spectrophotometer in the 4 000~600 cm^{-1} range. The crystal data were collected on a Bruker Apex Ⅱ CCD diffractometer. Thermogravimetric analysis (TGA) experiments were carried out on a NETZSCH STA 449F3 thermal analyzer from 40 to 800 ℃ under N_2 at a heating rate of 10 ℃·min^{-1}. The solid UV-Vis spectra were measured on a UV25500 UV-VIS-NIR Spectrophotometer (Shimadzu Corp.). Powder X-ray diffraction (PXRD) determinations was performed on an X-ray diffractometer (D/max 2500 PC, Rigaku) with Cu $K\alpha$ radiation (λ=0.154 06 nm). The crushed single crystalline powder samples were scanned at 40 kV (generator voltage) and 40 mA (tube current) from 5° to 50° with a step of 0.1°·s^{-1}. Emission spectra in the solid state at room temperature were taken on a Cary Eclipse fluorescence spectrophotometer.

1.2 Synthesis of $[La_2(dns)_2(Hdns)_2(phen)_4]$ (1)

A mixture of La_2O_3 (0.033 g, 0.1 mmol), H_2dns (0.069 g, 0.3 mmol), phen (0.060 g, 0.3 mmol), methanol (4 mL) and deionized water (8 mL) was sealed in a Teflon-lined stainless vessel (15 mL) and heated at 140 ℃ for 48 h under autogenous pressure. The vessel was then cooled by air cooling to room temperature spontaneously. Yellow and flake single crystals were obtained by filtration, washed with deionized water, and dried in air. Yield: 0.053 g (28%, based on La). Anal. Calcd. for $C_{76}H_{42}La_2N_{16}O_{28}$(%): C, 47.92; H, 2.22; N, 11.76. Found (%): C, 47.85; H, 2.15; N, 11.83. IR (KBr, cm^{-1}): 3 360(w), 3 078(w), 1 604(s), 1 577(s), 1 521(m), 1 492(s) 1 427(s), 1 318(s), 1 278(m), 1 169 (m), and 1 080(m).

1.3 Synthesis of $[La_4(dns)_6(phen)_6]$ (2)

The same procedure as that for **1** was used for complex **2** except the molar ratio of reactants. The amounts of reactants used in synthetic complex **2** are as follows: La_2O_3 (0.033 g, 0.1 mmol), H_2dns (0.046 g, 0.2 mmol), phen (0.080 g, 0.4 mmol). Yellow and flake single crystals were obtained by filtration, washed with deionized water, and dried in air. Yield: 0.046 g (31%, based on La). Anal. Calcd. for $C_{114}H_{60}La_4N_{24}O_{42}$ (%): C, 45.74; H, 2.02; N, 11.23. Found(%): C, 45.67; H, 1.95; N, 11.29. IR (KBr, cm^{-1}): 3 082(w), 1 600(s), 1 568(s), 1 516(m), 1 487(s), 1 425(s), 1 315(s), 1 273 (m), 1 163(m), and 1 083(m).

1.4 X-ray structure determination

Single-crystal X-ray diffraction measurements for complexes **1** and **2** were collected on a Bruker SMART APEX Ⅱ diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) at room temperature by using an ω-2θ scan mode. The structure was solved by direct methods with SHELXS-97 program[14] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97[15]. All non-hydrogen atoms were refined anisotropically. All the H atoms were positioned geometrically and refined using a riding model. In the crystal structure refinement of complex **1** some disagreeable reflections are omitted. The crystallographic data and selected bond lengths and angles are listed in Table 1 and Table 2, respectively.

CCDC: 1856530, **1**; 1856531, **2**.

Table 1 Selected crystallographic data for complexes 1 and 2

	1	2
Empirical formula	$C_{76}H_{42}La_2N_{16}O_{28}$	$C_{114}H_{60}La_4N_{24}O_{42}$
Formula weight	1 905.07	2 993.50
T / K	296(2)	296(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	1.190 83(3)	1.779 97(5)
b / nm	1.410 73(4)	1.862 85(5)
c / nm	1.415 04(4)	1.944 36(5)
α / (°)	62.154 8(6)	89.230 9(12)
β / (°)	73.243 9(7)	67.830 6(12)
γ / (°)	65.301 8(7)	74.219 9(12)
V / nm^3	1.896 78(9)	5.716 7(3)
Z	2	2
D_c / (g·cm^{-3})	1.668	1.739
Unique reflection	1.209	1.567
R_{int}	0.013 9	0.024 7
GOF	1.193	1.139
Final R indices [$I>2\sigma(I)$]	R_1=0.025 8, wR_2=0.071 2	R_1=0.036 8, wR_2=0.111 1
R indices (all data)	R_1=0.027 6, wR_2=0.073 4	R_1=0.052 4, wR_2=0.145 7

Table 2 Selected bond lengths (nm) and angles (°) in complexes 1 and 2

1					
La(1)-N(5)	0.281 48(18)	La(1)-O(1)	0.251 88(14)	La(1)-O(2)A	0.261 86(17)
La(1)-N(6)	0.272 74(18)	La(1)-O(3)	0.249 19(15)	La(1)-O(1)A	0.266 70(14)
La(1)-N(7)	0.279 82(18)	La(1)-O(8)	0.253 84(15)	La(1)-O(9)A	0.263 28(15)
La(1)-N(8)	0.276 05(19)				
O(3)-La(1)-O(1)	66.48(5)	O(3)-La(1)-O(2)A	176.61(5)	O(3)-La(1)-O(9)A	74.04(5)
O(3)-La(1)-O(8)	106.56(6)	O(1)-La(1)-O(2)A	110.45(5)	O(1)-La(1)-O(9)A	69.25(5)
O(1)-La(1)-O(8)	67.07(5)	O(8)-La(1)-O(2)A	70.52(6)	O(8)-La(1)-O(9)A	131.12(5)
2					
La(1)-O(60)	0.255 8(3)	La(2)-O(59)	0.238 5(3)	La(3)-N(6)	0.266 8(3)
La(1)-O(36)	0.255 9(3)	La(2)-O(32)	0.245 9(3)	La(4)-O(68)	0.242 5(3)
La(1)-O(33)	0.257 9(2)	La(2)-N(20)	0.267 8(3)	La(4)-O(45)	0.242 9(3)
La(1)-O(67)	0.258 1(3)	La(3)-O(54)	0.246 5(3)	La(4)-O(37)	0.249 3(3)
La(1)-O(47)	0.258 7(3)	La(3)-O(35)	0.243 9(3)	La(4)-N(11)	0.270 1(3)
O(60)-La(1)-O(36)	160.35(9)	O(59)-La(2)-N(20)	73.82(12)	O(54)-La(3)-N(6)	68.24(10)
O(36)-La(1)-O(33)	107.97(8)	O(35)-La(3)-O(54)	143.99(10)	O(68)-La(4)-O(45)	140.93(11)
O(59)-La(2)-O(32)	143.71(12)	O(35)-La(3)-O(34)	95.24(9)	N(11)-La(4)-N(10)	72.34(11)

Symmetry codes: A: $-x+1$, $-y+1$, $-z+1$.

2 Results and discussion

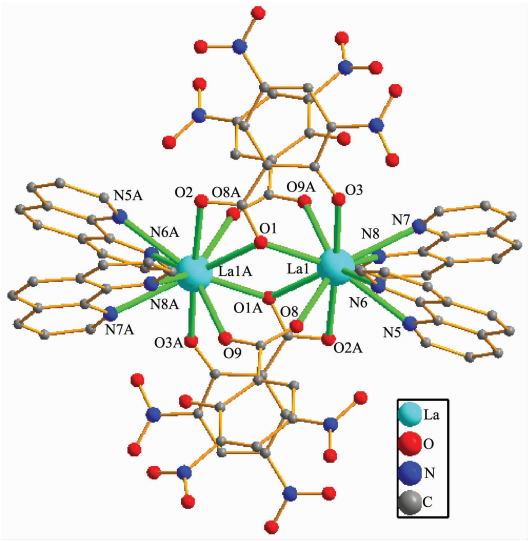
2.1 Synthesis

Complexes **1** and **2** have the same synthetic methods, except for different molar ratios of the reactants. In the syntheses of complexes **1** and **2**, phen can be used not only as the ligand but also as

the base to accept proton of H_2dns. In the synthesis of complex **1** the molar ratio of H_2dns to phen is 1∶1, whereas is 1∶2 for complex **2**. A suitable proportion of phen can make H_2dns lose two protons into dns and participate in coordination, such as complex **2**. Conversely, a low proportion of phen can only make part of H_2dns lose protons into dns or Hdns in complex **1**. It is easy to get pure crystalline complexes **1** and **2** instead of mixtures of **1** and **2** in the reaction. The different structures of complexes **1** and **2** indicate the La(Ⅲ) ions can form different thermodynamics controlled complex to meet the coordination environment of ligands.

2.2 Structure description of $[La_2(dns)_2(Hdns)_2(phen)_4]$ (1)

Complex **1**, $[La_2(dns)_2(Hdns)_2(phen)_4]$, crystallizes in triclinic $P\bar{1}$ space group. As shown in Fig.1, the molecule of **1** presents a butterfly structure. La(1) ion is coordinated by four nitrogen atoms from two phen ligands and six oxygen atoms from dns and Hdns ligands to form a $[LaN_4O_6]$ coordination geometry. La(1) and La(1)A are linked by dns and Hdns ligands and the La-La distances is 0.433 1 nm. The La(1), La(1)A, O(1) and O(1)A form the basal plane. In the structure, four 3,5-dinitrosalicylic acid ligands have two kinds of coordination modes: two of them lose one proton from carboxyl group and adopts didentate coordination modes; the others lose two protons from carboxyl and phenolic hydroxyl groups and adopts tridentate coordination modes (Scheme 1a and 1b). The phen molecules are parallel and the face-to-face distance is 0.354 0 nm, indicating the existence of the π-π stacking interactions.

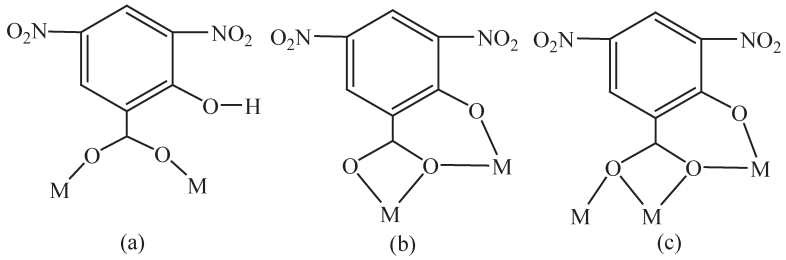


Hydrogen atoms are omitted for clarity; Symmetry codes: A: $-x+1, -y+1, -z+1$

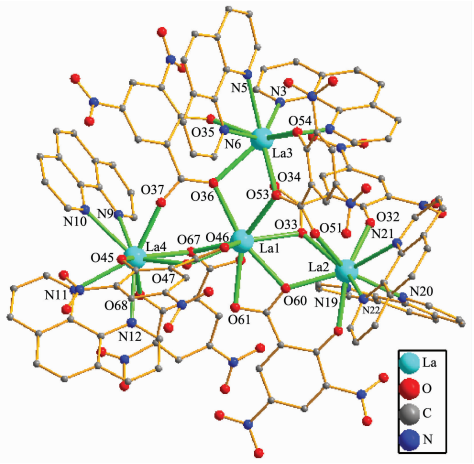
Fig.1　Molecular structure of **1**

2.3 Structure description of $[La_4(dns)_6(phen)_6]$ (2)

Complex **2**, $[La_4(dns)_6(phen)_6]$, also crystallizes in triclinic $P\bar{1}$ space group. As shown in Fig.2, there are four crystallographically independent La(Ⅲ) ions in complex **2** which form the basal plane. La(1) is nearly at the center of La(2), La(3) and La(4) and the La(1)-La(2), La(1)-La(3), La(1)-La(4) distances are 0.429 3, 0.411 9 and 0.429 2 nm, respectively. La(1) ion is coordinated with ten oxygen atoms from six dns ligands to from a $[LaO_{10}]$ coordination environment. La(2), La(3) and La(4) ions adopt the same $[LaN_4O_5]$ coordination environment where the four nitrogen atoms are from two phen ligands and five oxygen atoms are from three H_2dns ligands. Each 3,5-dinitrosalicylic acid ligand loses two hydrogen protons and adopts tridentate coordination modes. In the structure, there are two kinds of coordination modes among the six 3,5-dinitrosalicylic acid ligands (Scheme 1b and 1c). The four lanthanum ions were further linked together by six 3,5-dinitrosalicylic acid ligands to form the $[La_4]$ core.



Scheme 1　Coordination modes of Hdns and dns ligands in complexes **1** and **2**



Hydrogen atoms are omitted for clarity

Fig.2 Molecular structure of **2**

2.4 Powder X-ray diffraction analyses

The phase purity of compounds **1** and **2** was characterized by powder X-ray diffraction (PXRD) at room temperature. The pattern calculated from the single-crystal X-ray data of **1** and **2** were in good agreement with the observed ones in almost identical peak positions (Fig.3). The difference in reflection intensities between the simulated and experimental patterns was due to the powder size and variation in preferred orientation for the powder samples during collection of the experimental PXRD data.

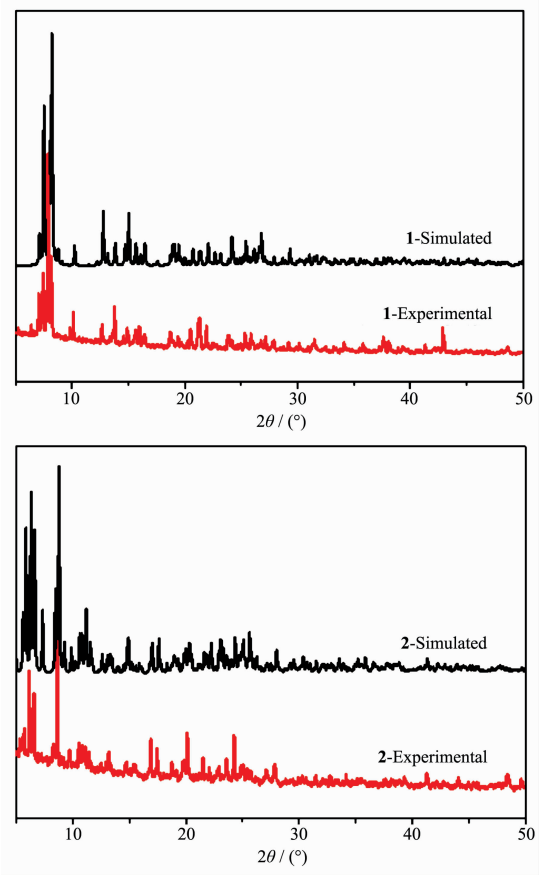


Fig.3 XRD patterns of complexes **1** and **2**

2.5 Thermal stability

Thermal stability is an important aspect for the application of coordination compound. Thermogravimetric analysis (TGA) experiments were carried out to determine the thermal stabilities of **1** and **2** (Fig.4). Complexes **1** and **2** are stable at less than 300 ℃ mainly because there are no free or coordinated solvent molecules in **1** and **2**. For complex **1**, the first consecutive step of weight loss in TG curves was observed in the range of 300~330 ℃, corresponding to the release of one dns ligand (Calcd. 11.97%; Obsd. 11.66%). Then, the continuously weight loss corresponds to the release of other ligands at about 398 ℃. When the temperature is higher than 400 ℃, the weight loss declines slowly and the total weight loss was about 75.74% at 900 ℃. For **2**, there is only one obvious process of thermal weight loss at about 390 ℃. When the temperature is higher than 390 ℃, the weight loss declines slowly and the total weight loss was about 65.57% at 900 ℃.

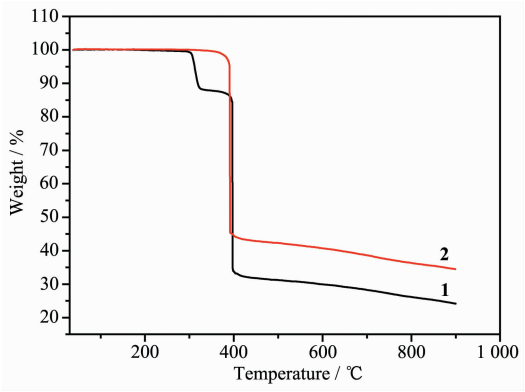


Fig.4 TGA of complexes **1** and **2**

2.6 Diffuse-reflectance UV-Vis spectra and photoluminescence properties

All UV-Vis absorption spectra of **1** and **2** as well as free ligand H_2dns and phen were recorded in the solid state at room temperature (Fig.5). In the absorption spectrum of phen, there were three absorption peaks (213, 254 and 332 nm) due to the K-band (the characteristic absorption band in the

conjugated bond), the B-band (the characteristic absorption band of aromatic compounds), and the R-band (the characteristic absorption band in the conjugated bond with heteroatom)[16], corresponding to the $\pi\rightarrow\pi^*$ or $n\rightarrow\pi^*$ transition transitions[17]. In the absorption spectrum of H_2dns, there were two absorption peaks (286 and 375 nm) due to the B-band and the R-band. The absorption peaks for **1** and **2** (212, 261 and 325 nm for **1**; 213, 262 and 325 nm for **2**) were very similar to the phen ligand, which may be assigned to phen ligand. The differences for complexes **1** and **2** compared with the phen may be attributed to the strong conjugation and inter/intra-molecular interaction between the molecule segments of ligands.

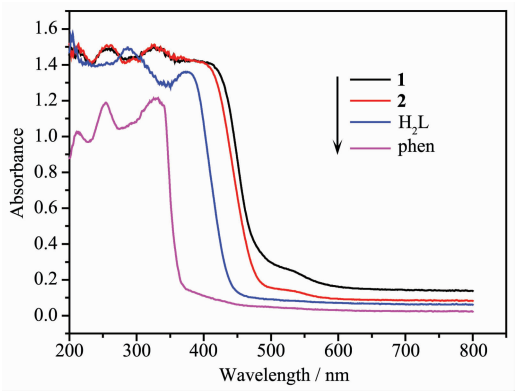


Fig.5 Solid UV-Vis absorption spectra for H_2dns, phen, **1** and **2** at room temperature

The solid-state photoluminesent properties of H_2dns, complexes **1** and **2** have been investigated in the solid state at room temperature (Fig.6). The emission spectrum of H_2dns ligand showed emissions at 450 nm (λ_{ex}=294 nm), which is probably attributable to the $\pi^*\rightarrow n$ or $\pi^*\rightarrow\pi$ transition[18]. It can be observed that the wavelength of emission spectrum of **1** and **2** is the same, except that the intensity of **2** was greater than **1**. Complexes **1** and **2** showed the same main peak at 467 nm (λ_{ex}=308 nm), which was similar to that of H_2dns, mainly originated from ligand-based luminescence. In contrast to the case for the free H_2dns ligand, the emission bands of complexes **1** and **2** red-shifted 17 nm, originated from ligand-to-metal charge transfer[19]. Furthermore, it's worth noting that the decrease of luminescence for complexes **1** and **2** compared with the free ligand H_2dns may mainly originate from the coordination interactions between the La (Ⅲ) ion and the ligands, which reduced conformational rigidity of complexes and then enhanced the non-radiative energy loss[20-21].

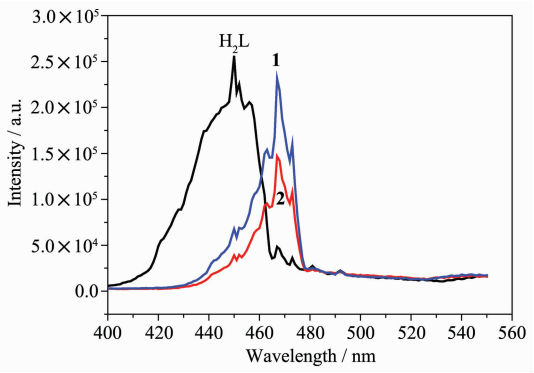


Fig.6 Emission spectra of H_2dns, **1** and **2** in the solid state at room temperature

3 Conclusions

In summary, two new La(Ⅲ) complexes $[La_2(dns)_2(Hdns)_2(phen)_4]$ and $[La_4(dns)_6(phen)_6]$ based on 3,5-dinitrosalicylic acid and 1,10-phenanthroline are prepared. The crystal structures and phase purity of the two complexes are characterized by single-crystal and powder X-ray diffraction. Furthermore, luminescent properties of these two complexes in the solid state at room temperature mainly originated from ligand-based luminescence of H_2dns, corresponding shifts originated from ligand-to-metal charge transfer.

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